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STUDIES ON REDUCTION OF NOBLE METAL SURFACE OXIDES IN RELATION TO ELECTROCHEMICAL OXYGEN REDUCTION

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1. INTRODUCTION AND STATUS OF THE WORK

The project originated from our interest in the role of surface oxides on the noble metals in regard to the kinetics of various electrochemical processes such as oxygen reduction at such metals. Initial aspects of the work were commenced at the end of a U.S. Army contract on hydrocarbon oxidation from which a number of papers (1 - 8) (which have been published or are in press) have originated. Work commenced on the present grant in July 1968 with Dr. H. Kozlowska as the research associate. Theoretical work was carried out in collaboration with Dr. Stonehart following earlier related work in this laboratory with Gileadi.

The three main aspects of the work that have been and are being developed in the present reporting period are:

a) Development of model experiments on reduction of Pt surface oxides at 25°C in relation to interaction effects and rearrangement processes in the surface layer;

b) Development of apparatus and technique for study of surface oxide formation and reduction at some noble catalytic metals and alloys at elevated temperatures up to 200°C in water at pressures above 1 atm ;

c) Analysis of the results by theoretical procedures based on the treatment of kinetic effects in transients.

Work from (a) and (c) is in preparation for publication.

Electrochemical oxygen reduction, particularly under optimum fuel cell conditions where polarization is to be minimized, proceeds in a potential region where chemisorbed oxygen species exist on Pt and Rh electrode surfaces. The kinetics of the process therefore involve such oxide species either as an inhibitor or a co-reactant intermediate. The study of the oxide species on Pt and other metals, in particular its reduction, is therefore of interest in regard to the mechanism of oxygen reduction. The effects of temperature on the reduction of surface oxide at Pt have been little studied and the general aims of the present work have therefore been concerned with this matter in relation to:

a) model studies at room temperature in $HClO_4$ and H_2SO_4 with Pt, Rh and Ir, in which oxide formation has been allowed to occur at (i) various controlled potentials in a short controlled (programmed)time period; and (ii) for various controlled periods of time at constant potential. Oxide reduction profiles were then obtained in linear cathodic sweeps. The results were analyzed by a theoretical procedure described in (b) below, and reported in more detail in the following pages.

b) the theoretical treatment of the reduction behavior of surface oxides was developed in collaboration with Stonehart following the theoretical work developed in this laboratory with Gileadi on rate effects in transients.

2. DEVELOPMENT OF PROCEDURES AND EXPERIMENTS FOR STUDY OF Pt SURFACE OXIDATION AND REDUCTION AT ELEVATED TEMPERATURES AND THE REDUCTION BEHAVIOR AT ROOM TEMPERATURE

(i) Room temperature experiments on hysteresis

Following an earlier paper[9] published from this laboratory, reduction studies were performed on surface oxides developed at smooth Pt, platinized Pt, Rhodium and Iridium. The main interest in reduction behavior arises (a) in relation to the hysteresis characterizing the processes of oxide formation and reduction; (b) in relation to the kinetics of the reduction of the supposed rearranged surface oxide species on Pt and Rh, since a similar reduction process may be involved in other fuel cell processes[10] including oxygen reduction; and (c) in relation to time effects associated with slow growth and rearrangement of the surface oxide at the noble metals. The purpose of the initial experiments at room temperature was to evaluate whether the extent of hysteresis between oxidation and reduction processes at Pt and Rh, which *increases* as the anodic potential is *raised*, is directly connected with the *potential* of surface oxidation or with the *greater extent* of oxide formation that occurs in a given time at such higher potentials.

This matter was resolved by conducting experiments both at varying limits of anode potential in a potential step followed by a linear cathodic sweep (or in single cycle Λ sweeps) and in a trapezoidal potential program where surface oxidation was allowed to proceed for controlled times at a series of selected constant potentials. In the following paragraphs, a more detailed description of the experiments is given and is based on material prepared jointly with Dr. Kozlowska in this laboratory and with Dr. Stonehart of the American Cyanamid Company for publication in a forthcoming paper[11]. Detailed references to previous work in the literature will appear in the paper to be published.

(ii) Experiments and results at room temperature

The kinetics of reduction and the hysteresis between the processes of formation and reduction of the surface oxide at Pt have been examined previously[9,12] and the ellipsometric behavior studied[13]. Similar hysteretic effects occur with Pd, Rh, Ni[14] and Ag. At Pt, Rh and Pd, the surface oxide species are electrochemically adsorbed over a broad range of anodic potentials (two types of species are probably involved in the anodic formation process and can be partially resolved in electrochemical experiments with Pt and Rh in alkaline solution) but the striking result is that the reduction peak is usually a single, almost symmetrical (see below) one except under conditions of fast reduction when two peaks can be resolved[9] by the differential galvanostatic technique developed in this laboratory. The behavior of the reduction peaks at Pt, Rh, Ir and Pd has been examined in the present work following the previous work at various reduction rates reported earlier (cf. ref. 9).

Surface oxidation and reduction experiments were performed under electrically programmed conditions using a Wenking short rise-time potentiostat. A Servomex LF 141 function generator capable of providing single ramp, repetitive triangular or trapezoidal potential-time profiles was employed. The current-potential relations were followed on a Tektronix oscilloscope or on a Moseley X-Y recorder with a high input impedance, cathode follower input stage.

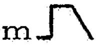
The cell and general technique used was identical with that employed in the work of Gilroy and Conway[9] described previously. Electrodes of the smooth metals were sealed in glass bulbs and the usual high purification techniques were employed. In other experiments, runs on platinized platinum were carried out.

The surface oxide species were allowed to form at potentiostatically controlled anodic potentials for known times (5 sec. to 600 sec.) at 25°C and were then reduced in successive transients at a fixed potential scan rate of 0.152 V sec.^{-1}. Electrodes were allowed to remain at +0.1 V (w.r.t. hydrogen electrode in the same solution) between each surface oxide formation and reduction experiment.

Typical potentiodynamic reduction profiles are shown in Fig. 1 for varying times of anodic polarization at the indicated potentials and in Fig. 2 for various anodic potentials in single Λ cyclic sweep experiments. The striking feature of all the results except those at Ir is that the *more anodic* is the polarization in the oxide formation process, the *more cathodic* is the potential of the peak, E_m, in the potentiodynamic reduction profile. Several experiments were designed, as mentioned above, to determine if this effect was caused directly by the higher potentials attained in the polarization or whether it was associated with the greater *extents* of oxidation which occur at the higher potentials due to growth of the oxide film. E_m is found to be related to the total charge q_r required for reduction of the oxidized surface. This is indicated by the results in Fig. 3 for Pt and in Fig. 4 for Rh where the relations between E_m and q_r are plotted for

(a) a series of single cycle (Λ) potentiodynamic polarizations to various anodic potentials,

and (b) for a series of reductions of films formed at two or three fixed potentials but for various times.

The dependence of E_m on q_r is almost the same (the slopes of the relations are almost identical) whether the E_m - q_r relation is obtained from rapid single cycle experiments, from time experiments with polarization extending up to 10 min. at each potential, or from potential step and single cathodic ramp experiments with a potential program of the form  . The range of q_r values extends from ca. 30 $\mu C.cm^{-2}$ (i.e. above the double-layer charging contribution) to ca. 800 $\mu C.cm^{-2}$ at Pt or to ca. 1800 $\mu C.cm^{-2}$ at Rh.

At Ir, by contrast, the area under the reduction profile, which in the linear potentiodynamic experiments is proportional to q_r, remains almost constant with both time or potential of polarization. At Pt[9] and Rh, and also at Pd, film growth evidently occurs to an extent related to potential and time but not at Ir. The growth behavior is logarithmic in time at Pt after short times, as shown previously[9, 14]; similar behavior is observed at Ni[15].

The possibility is to be recognized that the reduction profiles could become shifted due to polarization effects (cf. 9) because at a given scan rate, larger values of q_r will lead to greater reduction currents at all potentials including E_m. By performing reductions of the surface oxide at Pt from a given anodic potential held for various times but at scan rates adjusted so that the maximum currents at E_m were the same, it was possible to show that polarization effects could not account for the peak shifts observed. Very much larger ranges of scan rate are required[9] to show the polarization effect in the shift of the E_m and this was investigated previously[9]; such polarization effects are, as expected, logarithmic in sweep rate.

(iii) Reduction of Pt surface oxide at high temperatures

(a) General procedure and problems

Following the room temperature experiments summarized above, work was initiated on studies of the kinetics of Pt surface oxide reduction at elevated temperatures, with the anticipation of reaching temperatures up to 250°C in superheated water ($P \gg 1$ atm). The apparatus and experiments must, under these conditions, be set up and conducted in a high pressure bomb.

The necessity of using an airtight bomb for the experiments carried out at temperatures above 100°C posed two main problems: (1) the choice of a reference electrode, (2) the construction of a cell (I) which could fit into the small space inside the initially designed bomb having a diameter ca. 2"; a bomb having an i.d. of ca. 6" was constructed later and is shown in the accompanying photograph. Cell I (Fig. 5) consisted of coaxial counter (C) and working (W) compartments. The counter-electrode compartment in the outer vessel had a large platinized Pt gauze as an electrode. A small hole provided the necessary electrical contact with the inner working electrode compartment. The reference electrode was inserted into the upper end of a Luggin capillary tube placed inside the working compartment. The reference electrode was separated from the working compartment only by a thin asbestos wick which was found not to completely prevent diffusion between the two compartments. A smooth Pt wire was used as the working electrode. The temperature was measured by a thermistor placed into a tube in the working compartment. Before experiments were commenced, nitrogen was passed through both compartments, and the bomb, to remove oxygen. In a cell of this type, it is impossible to use the anion reference electrodes because diffusion of traces of heavy metal cations, e.g. Hg_2^{++}, to the Pt resulted in poisoning effects.

Test experiments showed that the quinhydrone electrode could not be used either because of diffusion and decomposition of quinhydrone at the higher temperatures, together with effects associated with depolarization of the Pt working electrode. On account of these difficulties, the Pd-H electrode was investigated; the Pt hydrogen electrode normally used cannot be employed in the bomb (but see below).

The Pd-H electrode: - Upon absorption of hydrogen, Pd can form a solid solution of α Pd-H and β Pd-$H_{0.6}$ phases. The potential of a Pd-H electrode with both phases present is constant and independent of the amounts of the phases. It could therefore be expected that a Pd-H[α + β] system will be able to maintain a constant potential for a long time even without H_2 in the solution provided that the concentration of β-phase is high enough. On the other hand, the concentration of the β-phase cannot be chosen too high because of the change of compositions of both phases which results with increasing temperature, a situation that can lead eventually to a single-phase system.

The following procedure was adopted for preparation of a Pd-H reference electrode: a Pd wire 0.26 mm. in diameter, 20 mm. length, 0.16 cm^2 area was spot-welded to a Pt wire which had benn previously sealed into a glass tube. The Pd was then annealed in a flame, the electrode transferred into the solution and reduced by cathodic polarization at a current density of 1.2 $mA.cm^{-2}$. The potential of the Pd-H electrode was measured against a platinized Pt hydrogen electrode in the same solution.

Isotherms: - The Pd electrode was polarized cathodically with a current of 1.2 $mA.cm^{-2}$ at 25°, 50° and 90°C and the potential was measured. The results are shown in Fig. 6. At the beginning of the polarization, the potential decreases rapidly, then slowly attains a constant value. It remains constant for a certain time and then slowly decreases again. The time interval in which the potential is constant becomes, however, shorter at higher temperatures.

As can be seen from Fig. 6, 3 h. is the most suitable time of polarization for forming the Pd-H for a current density of 1.2 $mA.cm^{-2}$. Connecting the points at the beginning of the constant-potential plateau and the points at the end, one obtains a bell-shaped curve corresponding to a phase diagram, representing the behavior of the α + β Pd-H phases.

(b) The temperature coefficient of the Pd-H electrode potential and preliminary results

The potential of the Pd-H electrode was measured at various temperatures in order to provide a basis for the kinetic studies using the Pd-H system as a reference electrode. The temperature was increased from room temperature to *ca*. 90°C and then decreased again to room temperature. The results are shown in Fig. 7. The potential of a fresh Pd-H electrode is found to have a value of about 55 - 60 mV. It rises slowly overnight to 66 - 68 mV. An increase of temperature above 40°C decreases the time of equalization of concentration and the potential attains its constant value faster. The potential is then linear with temperature until a temperature of *ca*. 80 - 90°C. At higher temperatures, however, it deviates from linearity returning to its previous value when the temperature is lowered again. The temperature coefficient in the 20 - 80°C range is -0.40 - -0.65 mV/°C. It is difficult to extrapolate these results to higher temperatures, however, and further work is needed here.

Preliminary measurements of the potentiodynamic V-i profiles on a smooth Pt electrode in 1 N H_2SO_4 solution were, however, made using the above Pd-H electrode as reference electrode.

The chosen potential range was:

1) for the most cathodic potential (a) the H_2 evolution potential or (b), in other measurements, a potential in the double-layer region 0.4V at Pt.

2) for the most anodic potentials - between 1.0 - 1.2 V. (Pt oxidized in this potential region giving a constant oxide reduction potential E_p).

The sweep rate was v = 0.125 V.sec.$^{-1}$ and typical results are shown in Fig. 8. The potential of the reduction peak apparently increases linearly with temperature (Fig. 5) with a slope of 0.40 mV/°C. The value of this coefficient shows that the main reason for the observed potential shift of E_p is the change of the reference potential of the Pd-H electrode. The significant uncertainty of both values, however, does not permit us yet to draw any final conclusions about the true temperature dependence of E_p at the present stage of the work. Further work is continuing.

An attempt was made to use the potential of H_2 evolution during the potential sweeps at the working electrode or the potential of the first hydrogen adsorption at Pt as a reference potantial but the results were not encouraging. At higher temperatures, it becomes difficult to distinguish the above mentioned processes on a sweep diagram and, at temperatures below 100°C, the temperature coefficients of E_p vary with the reference potential chosen, which indicates that these (internal) reference potentials are themselves temperature dependent as may be expected (cf. the finite heat of electrochemical adsorption of H).

In order to be able to evaluate the temperature coefficient of the reduction peak potential E_p it is clear that a very stable and reproducible reference electrode is required. One could expect that the dynamic (or autogenous) hydrogen electrode developed by Giner (i.e. a platinized Pt electrode on which hydrogen is evolved with practically no over-voltage at a very low c.d.) would be satisfactory. This electrode can be used only in a cell with both working and reference electrode compartments separated so that the reference electrode compartment can be staurated with H_2 without H_2 diffusing to the working electrode. This H_2/Pt electrode system also has a theoretical advantage insofar as the individual temperature coefficient can be calculated from the known entropies of H^+ (-5 ± 0.5 e.u.) and H_2, although the individual electrode potential cannot be known more accurately than *ca.* ± 0.5 V.

A second cell was therefore constructed (see photos) with the reference and working compartments separated by a solution wetted joint. To enable the reference electrode to be polarized, an auxiliary anode was placed above the reference electrode. Preliminary experiments showed that the whole arrangement could be more satisfactorily set up in a larger bomb. A high pressure stainless steel autoclave bomb was therefore purchased and a heating furnace was built around it. Electrical and high pressure gas fittings were attached. The head of this bomb allows six electrical leads to be passed into the vessel.

The new apparatus in which continuing work is proceeding is shown in the photograph and can accommodate a larger and more convenient cell which is now being tested and used. Preliminary runs have been conducted in the temperature range 125 - 150°C, and the latest measurements up to 190°C.

3. THEORETICAL EXAMINATION OF THE REDUCTION BEHAVIOR

Kinetic equations for potentiodynamic processes

The potentiodynamic method of examining electrode processes has become widely used but its basis in terms of kinetic effects in potentiodynamic transients has not yet been thoroughly examined. Part of the work here has therefore been concerned (in collaboration with Stonehart) with developing the necessary theoretical treatment for application to the results.

For reversible processes, the potentiodynamic behavior of species electrochemically adsorbed or desorbed, e.g. in a Faradaic adsorption, or surface-phase removal process, such as

$$X^- + M \underset{k_c}{\overset{k_a}{\rightleftharpoons}} MX + e$$

can be described in terms of the potential-dependent pseudo-capacitance[15] C_ϕ where the potentiodynamic current for a sweep rate v is

$$i = C_\phi v$$

In an irreversible or partially irreversible process (it is to be noted that all processes must eventually become irreversible depending on the overpotential and the exchange current), it is necessary to consider the individual currents for forward and backward directions of the process in the following way (cf. Srinivasan and Gileadi[16]).

It is assumed that the rate of the electrode reaction is the usual exponential function of the electrode potential and that the observed rate (current density) is the difference between the velocities of the forward and reverse reactions. For an electron transfer process in the absence of reactant replenishment and an initial electrode surface coverage q_o of electroactive reactant expressed in terms of Faradaic equivalents cm^{-2}, the surface coverage will be q_t at time t (sec) given by

$$q_t = q_o - \int_o^t i.dt \qquad (1)$$

If the rate of the reverse reaction is negligible compared with that of the forward reaction and if it is assumed for the present that there are no effects due to heterogeneity of the surface, then the kinetic equation for the process under potentiodynamic control may be written in terms of the time-dependent current i_t as

$$i_t = AkF\,[q_o - \int_o^t i\,dt]^m \,.\, \exp \frac{\alpha nF}{RT}\,(E^1 - E_o + vt) \qquad (2)$$

where i, A, n, F, R, T, and α have the usual electrochemical significance, k is the specific rate constant (cathodic or anodic) at a standard electrode potential, E_o, and m is the reaction order with respect to the adsorbed reactant. E^1 is the electrode potential at time t = 0 in a linear potential scan at rate, $\frac{dE}{dt}$ (= v volt sec.$^{-1}$).

A more general equation may be used to describe the kinetics of adsorbed reactants by including terms for the reverse reaction and also factors for the surface heterogeneity[16] as considered previously by Conway and Gileadi. The latter type of factor takes into account the common observation that the rate of reaction for surface species usually depends on the distribution of heats of activation over the sites involved in a heterogeneous surface so that the rate constant depends on the surface coverage of the electrode. The rate may then be an exponential function of the surface concentration as well as of potential, so that in the general case, for cathodic (rate constant k_c) and anodic (rate constant k_a) partial processes, the total net current is given by:

$$i = AF(k_c[q_o - \int_o^t i\,dt]^m \,.\, \exp \frac{\alpha nF}{RT}\,(E^1 - E_o + vt) + g\Theta \; -$$

$$k_a . \int_o^t i\,dt.\ \exp \frac{(\alpha - 1)nF}{RT}\,(E^1 - E_o + vt) - g'\Theta \qquad (3)$$

where the surface heterogeneity factor, g, will operate with respect to the fractional surface coverage, Θ. For situations where the dependence of heats of activation on coverage of surface sites is not great, then g → O, and the adsorption characteristics approach those expressed by Langmuir's relation.

Under potentiodynamic control, the reaction rate for an electrochemical desorption process exhibits a maximum due to the opposing effects of increasing potential on the rate and decreasing surface coverage of the reactant (equation 2). The shift of the potential of the maximum E_m with scan rate, v, can be used to obtain the transfer coefficient, α, as was examined experimentally for Pt surface oxide reduction[9] described previously. The treatment for interpretation of shift of E_m with scan rate, v, in terms of α strictly applies only when the reverse reaction term in eqn. 3 can be neglected. In the absence of the surface heterogeneity term, equation (3) then obviously approximates to equation (2).

Another indication of the reduction behavior is the shape of the potentiodynamic current-voltage peak; the latter may be characterized by the coverage of species remaining on the electrode surface, $q_{i,max}$, at the potential of maximum current, $i_{max.}$; i.e. by the asymmetry of the peak. In the case of an irreversible first-order reaction, then $q_{i\ max} = 0.37\ q_o$, and an asymmetric peak results. It is found that symmetric peaks are obtained for irreversible second-order reactions with $q_{i\ max} = 0.5\ q_o$, and the peak potential shifts with scan rate. Symmetric peaks are also obtained for the quasi-equilibrium situation where the contribution from the reverse reaction term can be considerable. In the latter case, however, the peak potential does not shift with scan rate. Finally, broad symmetrical peaks are obtained for irreversible reactions when $g \rightarrow 0$, the symmetry and peak-broadening being dependent upon the magnitude of g[17]. Herein lies the basis for distinction between various models proposed for any reaction.

Equation (3) cannot be solved analytically so numerical solutions were obtained on an SDS 930 computer and the effects of varying the parameters v, k_a, k_c, Θ, α and g were investigated. The difference between the kinetic behavior for several models with change of scan rate was determined for the first order ($m = 1$ in equation 2) irreversible situation, for the second order irreversible situation, and for the first order quasi-equilibrium situation ($m = 1$ in equation 3, $g = 0$). The results will be shown in detail in the paper in preparation[11] where the dependence of shape of the reduction profiles on g will be presented.

4. FORM OF THE EXPERIMENTAL REDUCTION PEAKS AND THE HYSTERESIS EFFECT WITH SURFACE OXIDE AT Pt

The progressive shift of peak potential which is observed with increasing extent of surface oxidation as measured by the charge q_r required for reduction of the oxide film can be interpreted in two ways which are to be regarded as complementary rather than alternative: (a) there is a progressive change in the g factor with time which changes the degree of asymmetry of the curves, so that the relative positions of the maxima are changed with q_r and hence with time/or potential of prior anodic polarization; (b) there is a progressive change of the E_o for the film determined by re-arrangement (cf. 13, 14) of the Pt and O species from an ad-layer type of arrangement to a two-dimensional "Pt-O-Pt" surface phase. The latter type of situation is required to explain the totally irreversible nature of the oxide formation and reduction processes which arises (except at very small coverages) independently of the rate of the formation or reduction process[9] and characterises the hysteresis.

The profiles for Pt surface oxide reduction were examined in detail on the basis of equation (3). The parameters of best fit for k_c, α and g (q_o is determined by the experimental total degree of surface oxidation) are tabulated below for several families of experimental curves obtained at different anodic potentials E. The parameter, g, characterizing the heterogeneity, progressively decreases with time as q_o increases. This seems reasonable, since with increase of q_o, the reduction becomes more one of a surface phase of significant thickness than one involving a monolayer, or less, of adsorbed species where heterogeneity effects may be expected to be more significant. The shapes of the curves of best fit for one family of experimental data (Pt. IV) are shown in Fig. 9.

The possibility that asymmetry arises from film resistance effects was also considered but assumption of a resistance equivalent to 0.1×10^{-6} ohm per monolayer cm^2 was shown to lead to far too much asymmetry to be an explanation for the observed behavior.

As the film becomes extended beyond a nominal monolayer ($q_r = 420\ \mu C\ cm^{-2}$ real area; $q_o/q_H = 2$), it may be anticipated that its free energy (per mole of ad-species) may decrease owing to rearrangement of Pt and O or OH species into first a two-dimensional surface phase and then into the initial stages of a three-dimensional phase. Very approximately, the free energy of the layer may be expressed in terms of three components: G_1 the free energy of the layer next to the metal, G_3 the free energy of the exterior layer adjacent to the solution and G_2 the free energy of any intermediate layers. At Pt, the O:Pt ratio at high potentials approaches a value of ca. 2 while at Rh and Pd it can become substantially larger so that in such cases G_2 can become significant. The growth of the oxide film may occur in patches (cf. the behavior at Ni) in which case the thickness will not be uniform. In any transformation from an initial ad-layer to a progressively thickening film or to patches[9] of locally thicker material, it seems reasonable to expect that the free energy of the surface oxide may suffer a decrease so that in the quasi-equilibrium situation, the E_o will become less positive to an extent related to q_r. This would also account for the hysteresis if an irreversible transformation to a more stable surface layer by rearrangement processes occurs.

At Pd, where reduction profiles taken from successively increasing anodic potentials are found to fall almost outside of each other, but are nevertheless symmetrical, the explanation must, it seems, be based on a changing value of E_o as the film thickens. For polarizations at 3 V. for extended periods of time (30 sec.), two peaks can be resolved in the reduction curve. The fact that for shorter polarization times, smooth symmetrical curves can be obtained, indicates that the surface species reduces as a single entity and not in distinguishable stages. For example, once a layer thicker than a monolayer has been layed down in some re-arranged form, reduction back to "zero coverage" does not reveal any region characteristic of a distinguishable monolayer. This again suggests reduction in ("hemispherical")patches rather than reduction by stripping of layers one by one from a plane surface phase of small but finite extension.

The results at Ir seem to indicate that with that metal, no re-arrangement or growth processes (in fact, the two effects are probably inter-connected) can occur at the temperature of the present experiments.

Adsorption Peak		αn	$(1 - \alpha)n$	k_a	k_c
I.	Anodic	0.445		1×10^{-3}	1×10^{-3}
	Cathodic		3.5		
II.	Anodic	0.745		2×10^{-3}	2×10^{-3}
	Cathodic		3.97		

In the case of Pt and Rh, the linear dependence of E_m on total q_r independently of whether the film is thinner or thicker than a nominal monolayer is a surprising result; similar behavior was found at Ni.

Table of Values of Parameters of Best Fit for Experimental Potentiodynamic Oxide Reduction Curves at Pt

E	Curve No. Pt. III	t	g	k_a	α	q_o	gq_o
1.147	2	7.5	3.81	0.21	0.26	76	291
	4	15	3.4	0.12	0.33	109	373
	6	65	3.65	0.044	0.42	149	544
	9	605	2.9	0.018	0.48	201	589
1.270	Pt IV						
	1	5	1.27	0.19	0.31	184	235
	3	10	0.87	0.14	0.35	268	233
	5	25	0.63	0.12	0.37	317	201
	7	125	0.54	0.079	0.40	379	206
	9	605	0.50	0.046	0.44	434	218
1.379	Pt II						
	1	5	0.84	0.092	0.40	299	253
	3	10	0.47	0.076	0.42	392	183
	5	25	0.37	0.069	0.41	431	158
	7	125	0.29	0.049	0.43	489	143
	9	605	0.21	0.039	0.44	534	111
1.527	Pt I						
	1	5	1.47	0.021	0.47	129	190
	3	10	0.48	0.020	0.44	158	75.5
	5	25	0.13	0.021	0.42	176	23.3
	8	305	-0.46	0.03	0.39	199	-92.5

The magnitudes of k_a and k_c are equivalent because E_o was chosen to be the potential at the quasi-equilibrium maximum for each reaction. For any other E_o chosen that does not coincide with the quasi-equilibrium maximum, then k_a and k_c will change, but their product will always be constant for a given set of data. Hence, the absolute magnitude of $k_a . k_c$ determines at what scan rate, v, the transition from quasi-equilibrium to irreversible behavior will tend to occur.

5. SOME GENERAL CONCLUSIONS

An analysis of the behavior of reaction rates for adsorbed oxygen species using the potentiodynamic perturbation technique shows that specific rate constants for formation and reduction processes may in favorable cases be determined quantitatively.

Surface heterogeneity terms in the kinetic equations can have a large effect on the kinetics so that selection of the correct reaction model can be difficult with limited experimental data. The differences between models can be distinguished, however, by a careful examination of the shape of the current-voltage curve and the behavior of the reaction rate maximum, i_{max}, with the scan rate, v, investigated, for example, by Gilroy and Conway at Pt[9].

The approaches developed and tested on results obtained at room temperature will be applied to the high temperature experimental data when they are satisfactorily reliable.

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FIGURE 1

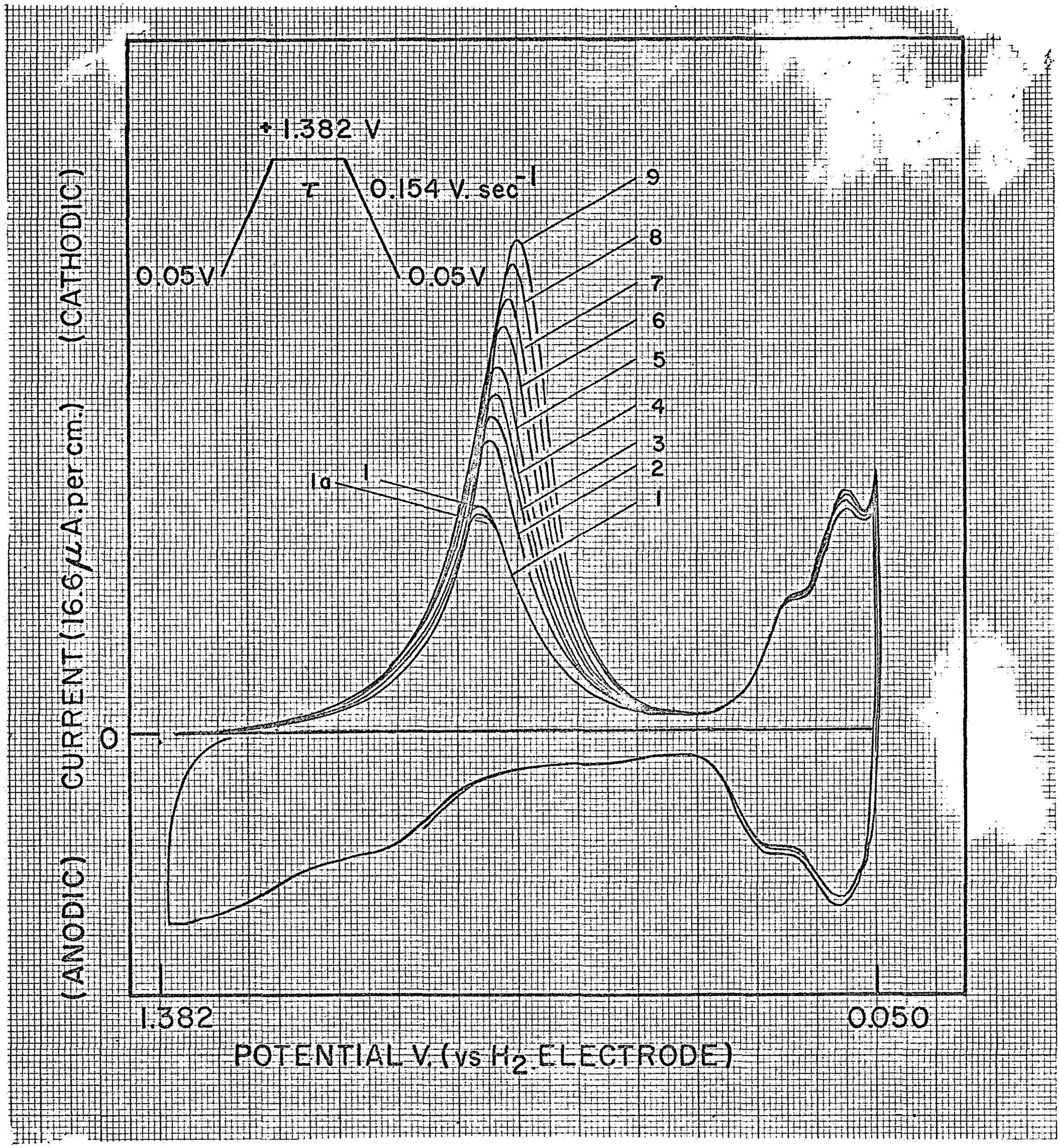
(a) Potentiodynamic reduction profiles for smooth Pt surface oxide formed for various times τ at 1.382 V. (1M aq. $HClO_4$, 25°C).

(b) Potentiodynamic reduction profiles for oxide at platinized platinum formed for various times τ after potential step to 1.45 V (1M aq. $HClO_4$, 25°C).

(c) As in 1a and 1b but for Rh at 1.287 V.

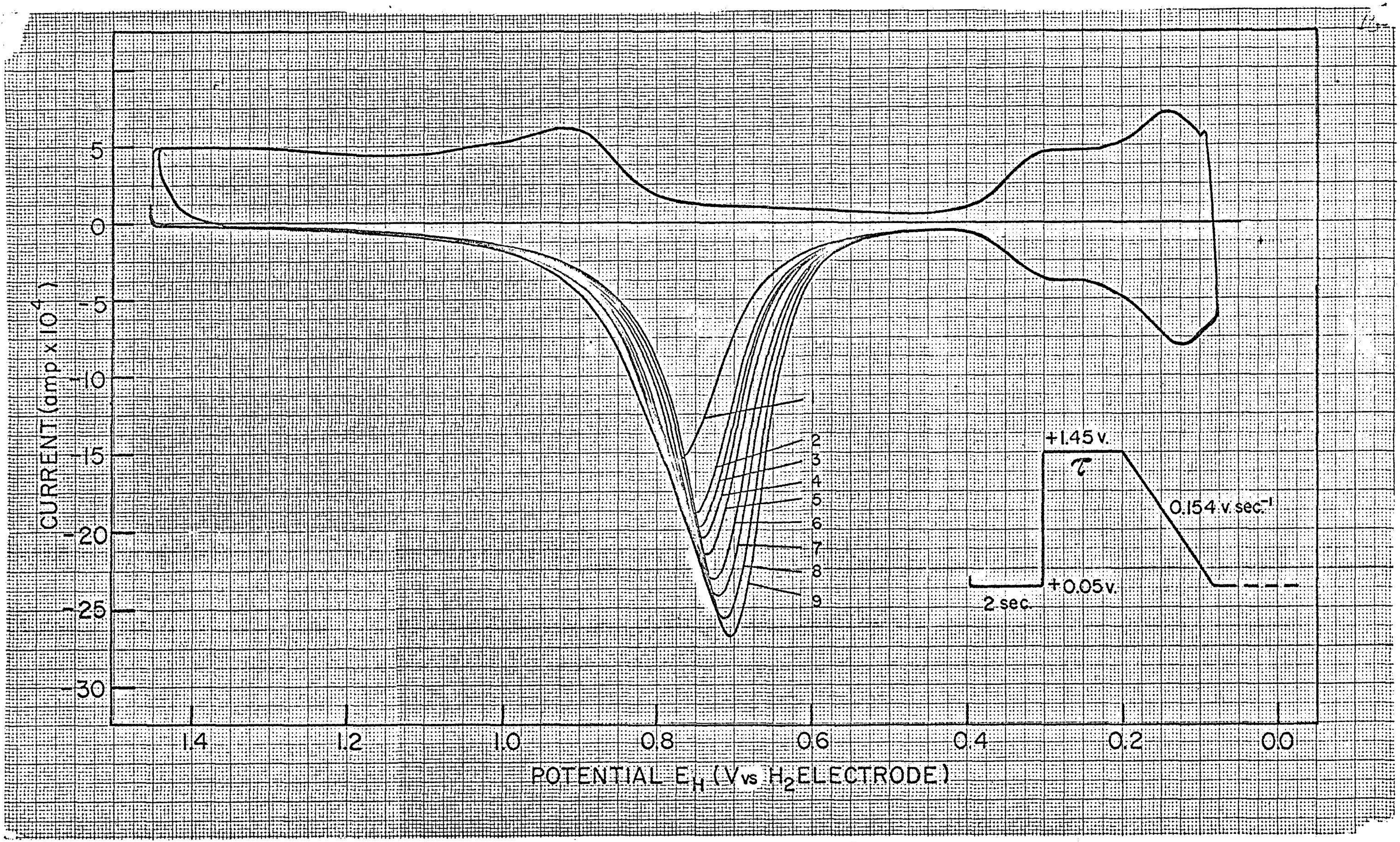
(d) As in 1a and 1b but for Ir at 1.18 V.

(a)

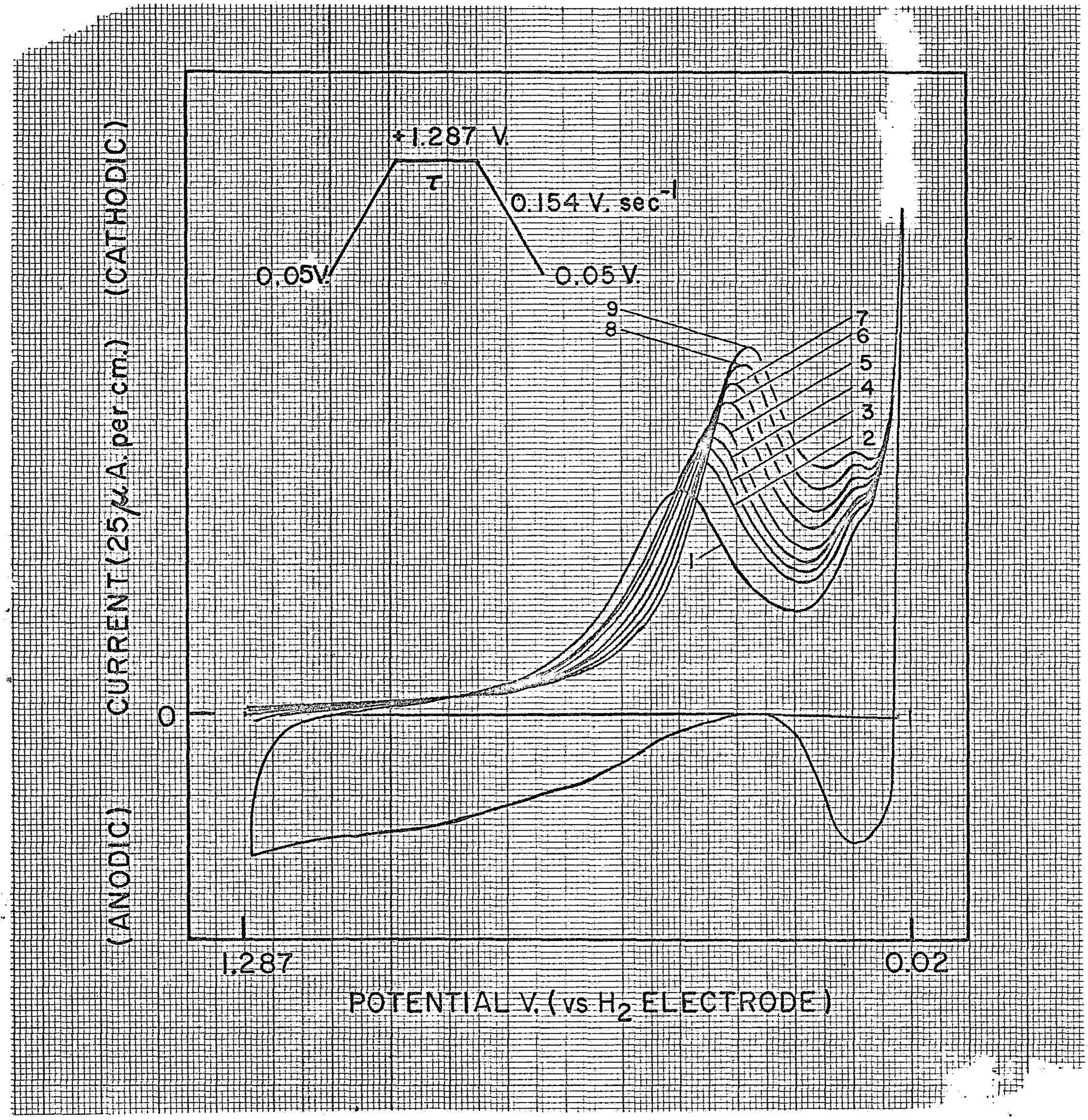


+1.382 V
τ
0.154 V. sec^{-1}
0.05V
0.05V
9
8
7
6
5
4
3
2
1
Ia
I
(ANODIC) CURRENT (16.6 μA. per cm.) (CATHODIC)
0
1.382
0.050
POTENTIAL V. (vs H_2 ELECTRODE)

(b)

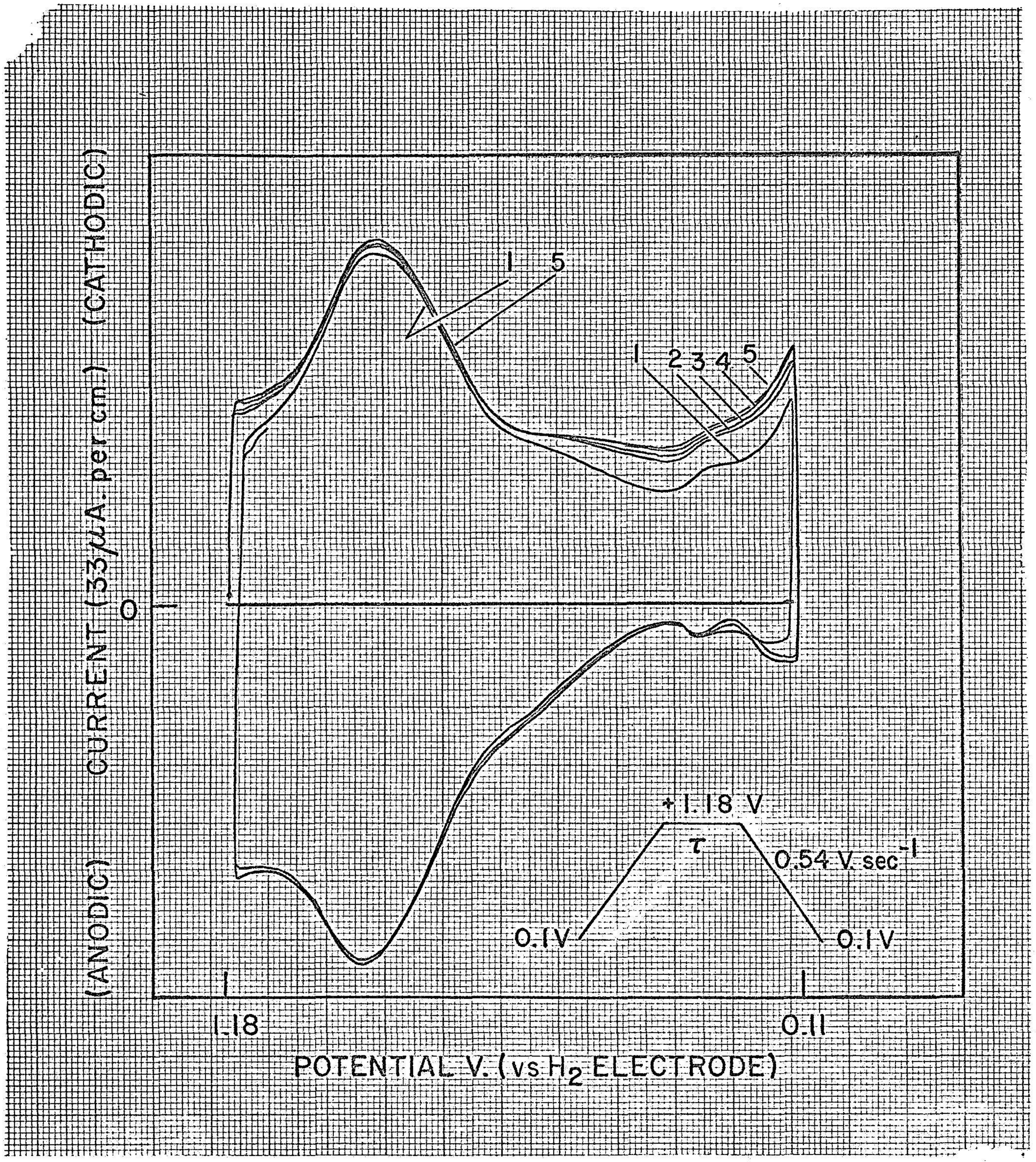

CURRENT (amp x 10^{-4})
5
0
-5
-10
-15
-20
-25
-30
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
POTENTIAL E_H (V vs H_2 ELECTRODE)
2
3
4
5
6
7
8
9
+1.45 v.
τ
0.154 v. sec.$^{-1}$
+0.05 v.
2 sec.

(c)



+1.287 V.
τ
0.154 V. sec^{-1}
0.05V.
0.05 V.
9
8
7
6
5
4
3
2
1
0
CURRENT (25 μA. per cm.)
(CATHODIC)
(ANODIC)
1.287
0.02
POTENTIAL V. (vs H$_2$ ELECTRODE)

(d)



1
5
1
2
3
4
5
0
CURRENT (33 μA. per cm.)
(CATHODIC)
(ANODIC)
+1.18 V
τ
0.54 V. sec^{-1}
0.1 V
0.1 V
1.18
0.11
POTENTIAL V. (vs H_2 ELECTRODE)

FIGURE 2

Potentiodynamic reduction profiles for smooth Pt surface oxide formed in single cycles to various anodic potentials. (1M aq. $HClO_4$, 25°C) (curves 1 - 6); limits E_x indicated by max. anodic potentials reached at left-hand side).

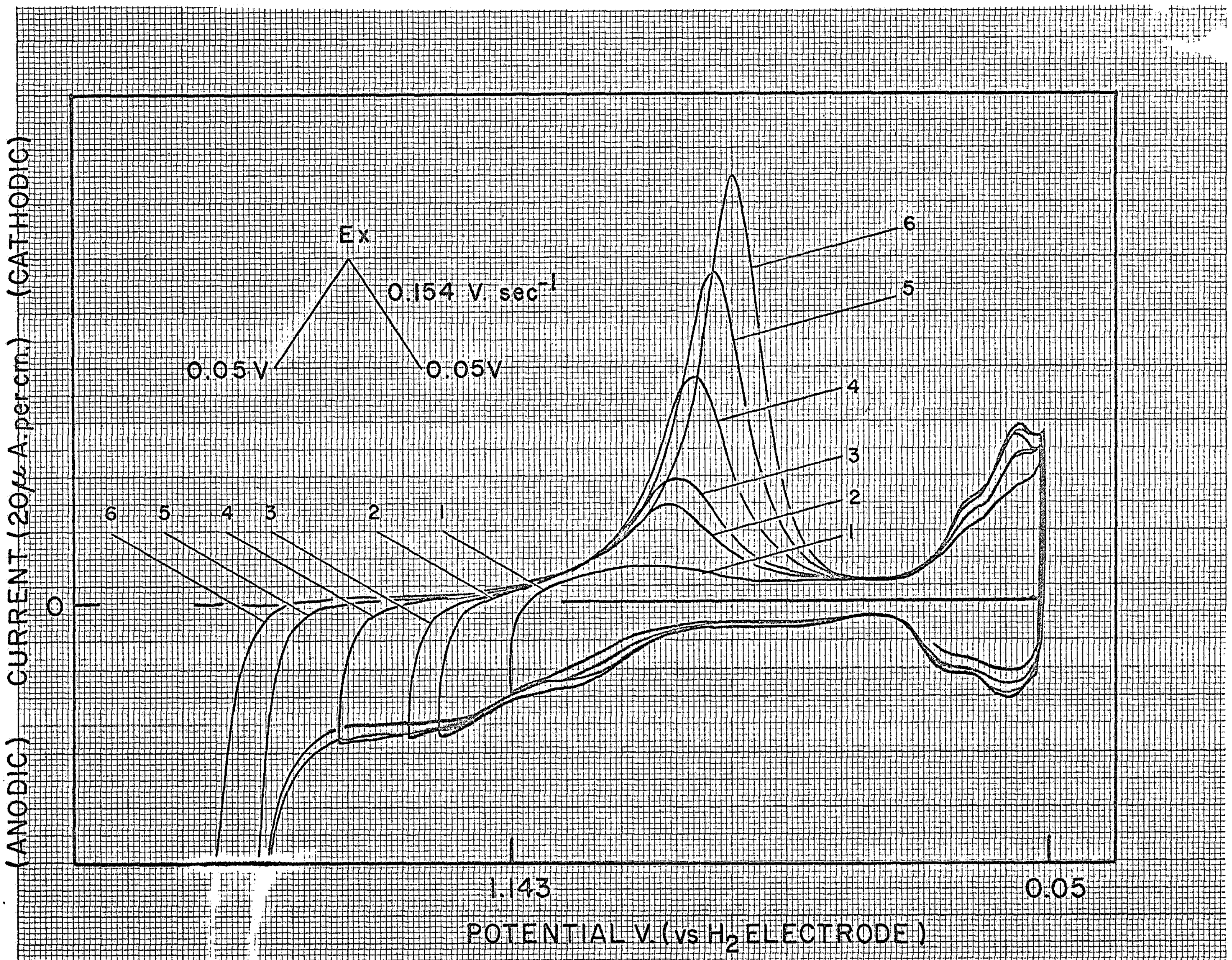
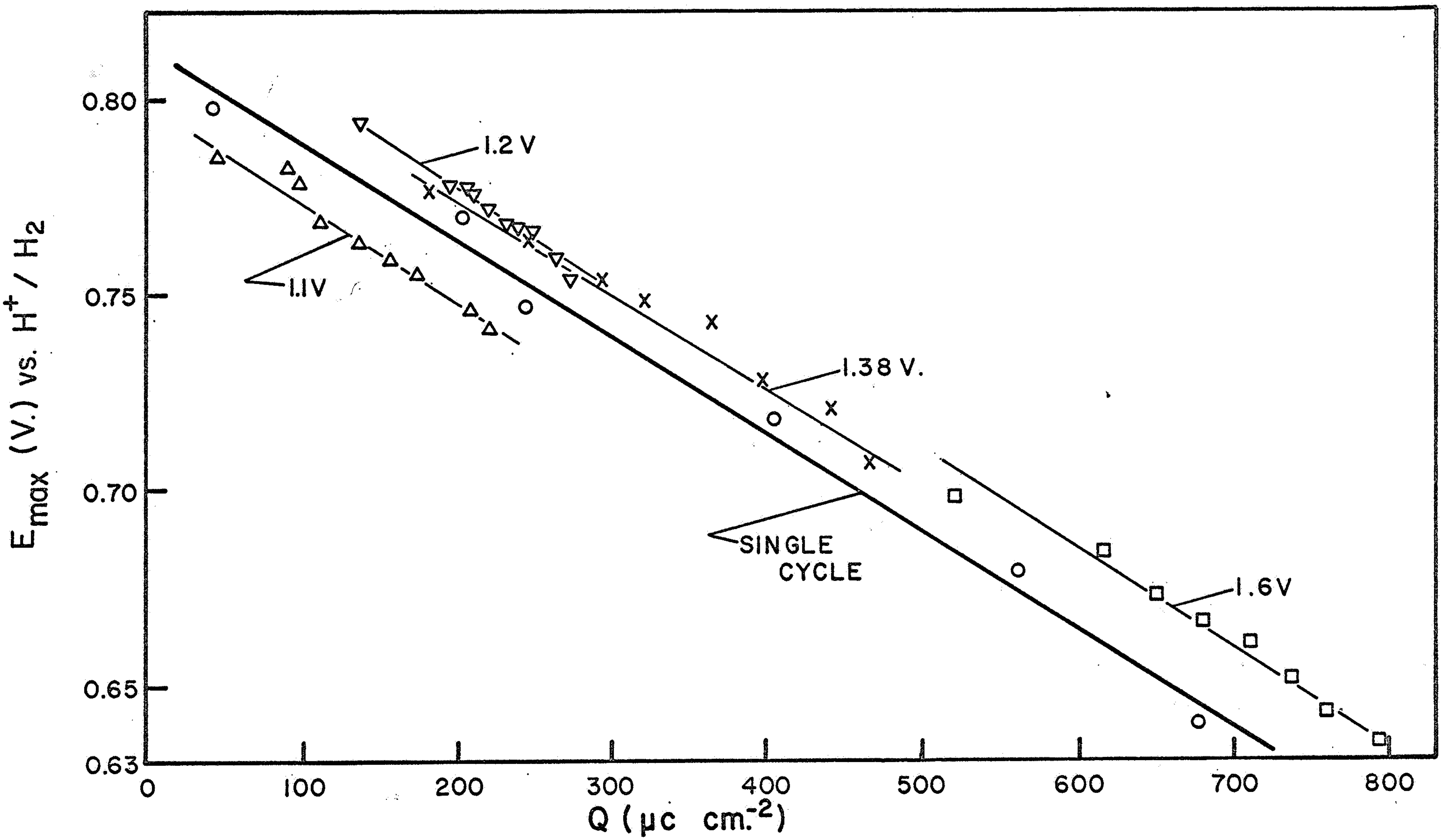

Ex
0.154 V. sec^{-1}
0.05V
0.05V
6
5
4
3
2
1
6
5
4
3
2
1
0
1.143
0.05
POTENTIAL V. (vs H_2 ELECTRODE)
(ANODIC) CURRENT (20μ A. per cm.) (CATHODIC)

FIGURE 3

Relations between potential of the reduction peak and the total reduction charge q_r for surface oxide at Pt. Heavy line: single cycle experiments as in Fig. 2; individual lines: reduction after growth for various τ at the indicated potentials.



0.80
0.75
0.70
0.65
0.63
E_{max} (V.) vs. H^+ / H_2
0
100
200
300
400
500
600
700
800
Q (μc cm.$^{-2}$)
1.2 V
1.1V
1.38 V.
SINGLE CYCLE
1.6V

FIGURE 4

As in Figure 3 but for Rh.

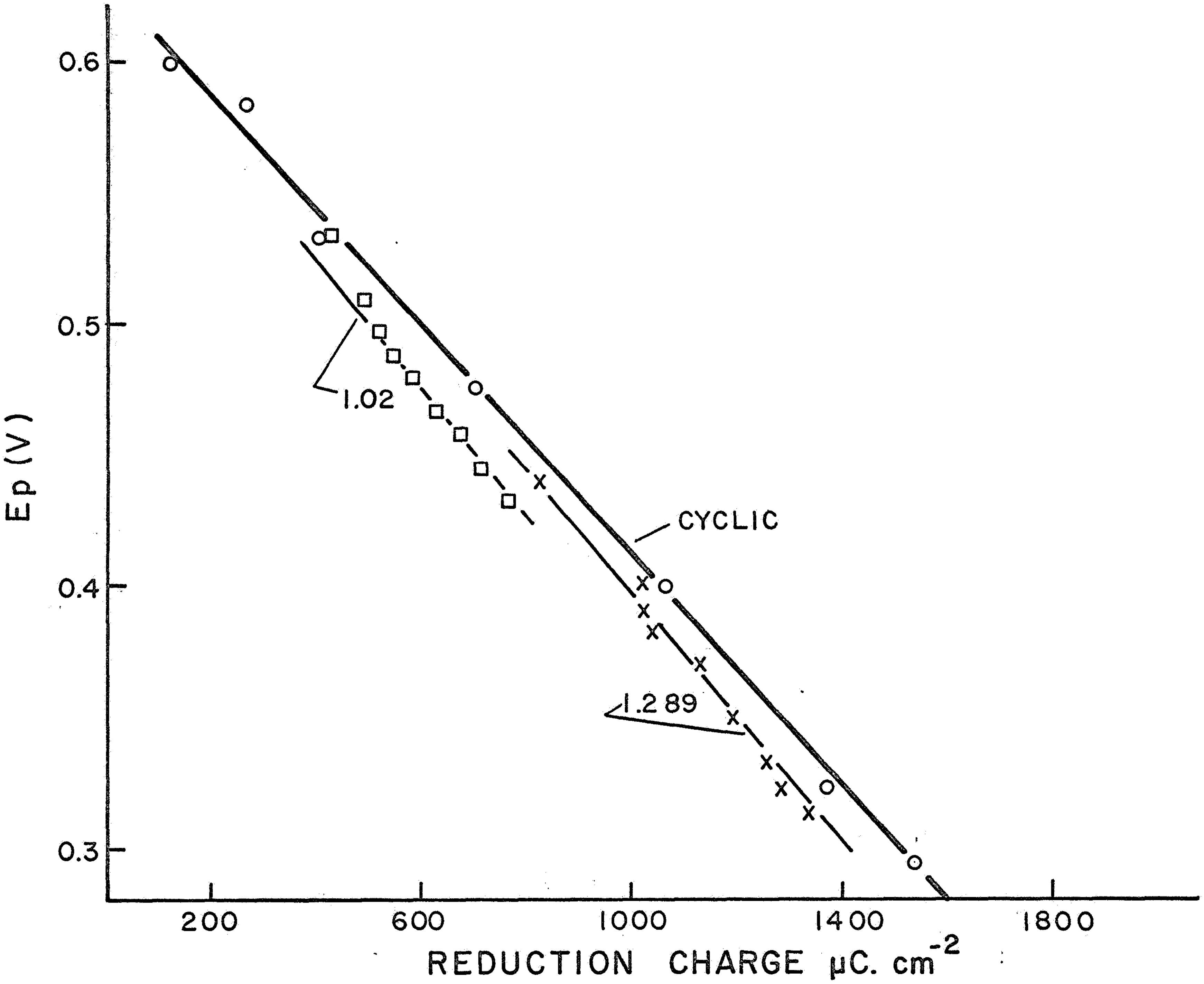

0.6
0.5
0.4
0.3
Ep (V)
200
600
1000
1400
1800
REDUCTION CHARGE μC. cm^{-2}
CYCLIC
1.02
1.289

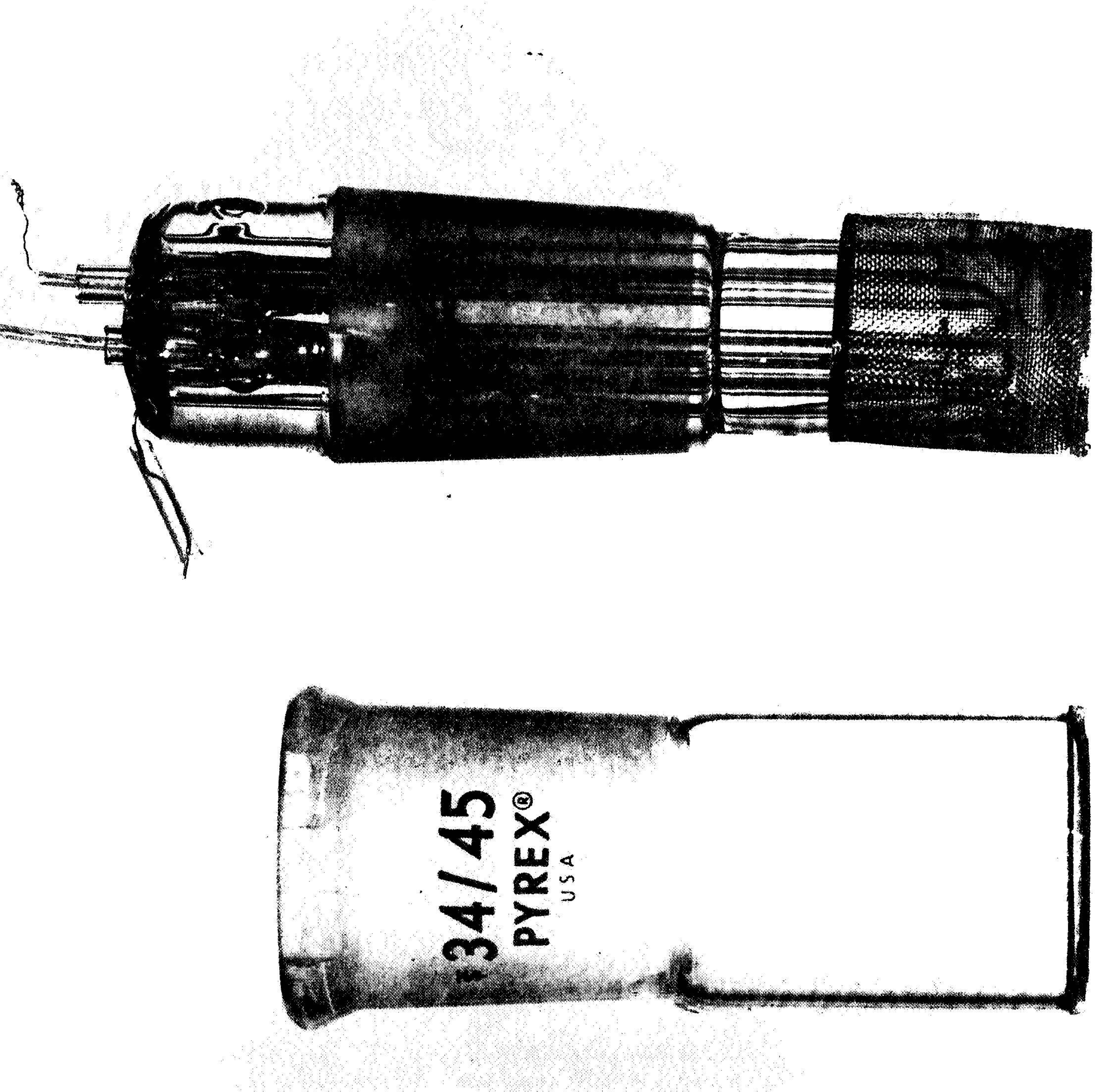
FIGURE 5

(a) Photo of first cell (I) for high temperature studies.

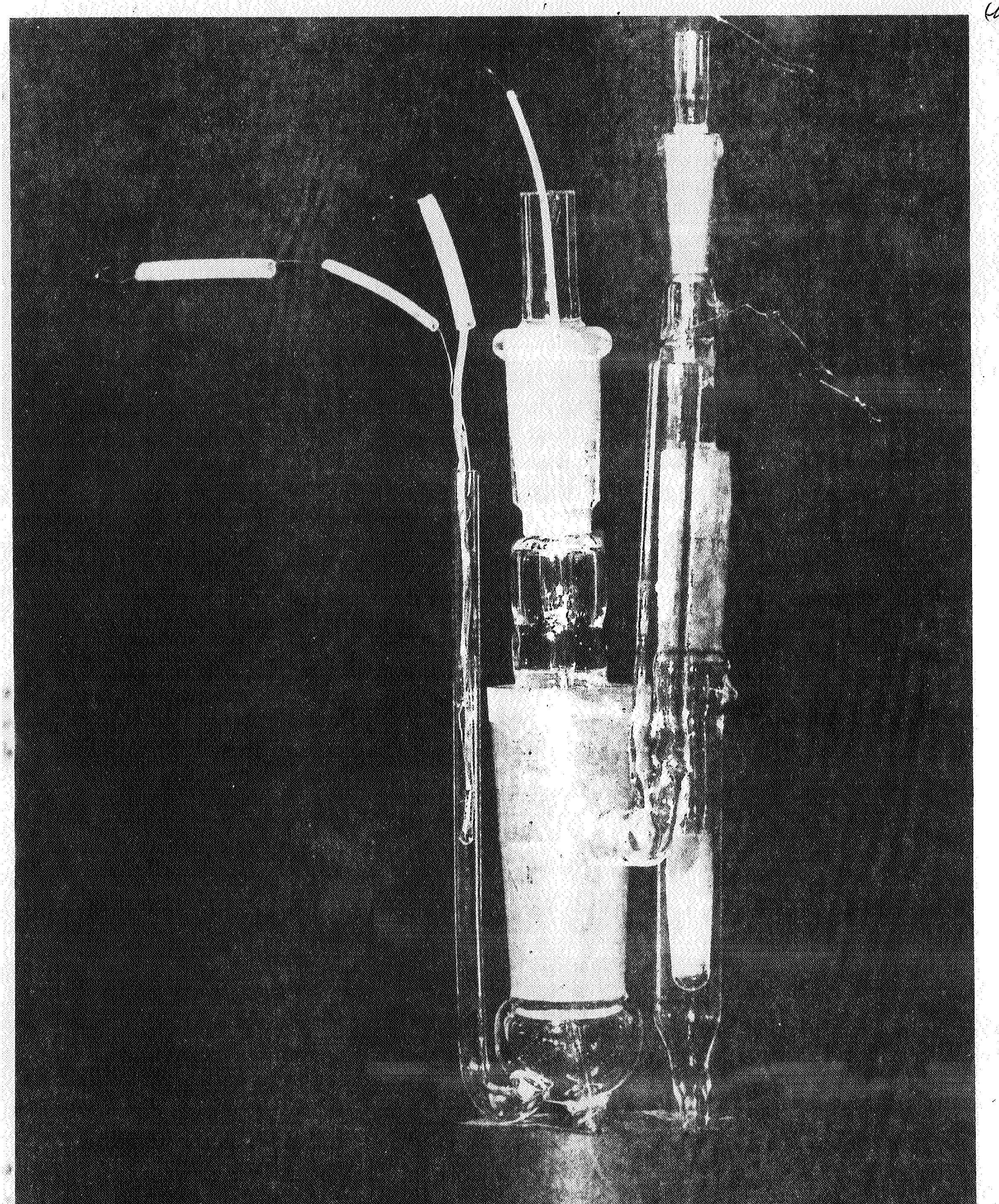
(b) Photo of improved micro-cell with separated compartments.

(c) Photo of new larger high temperature bomb.

(a)


34/45
PYREX®
USA

(b)



(c)

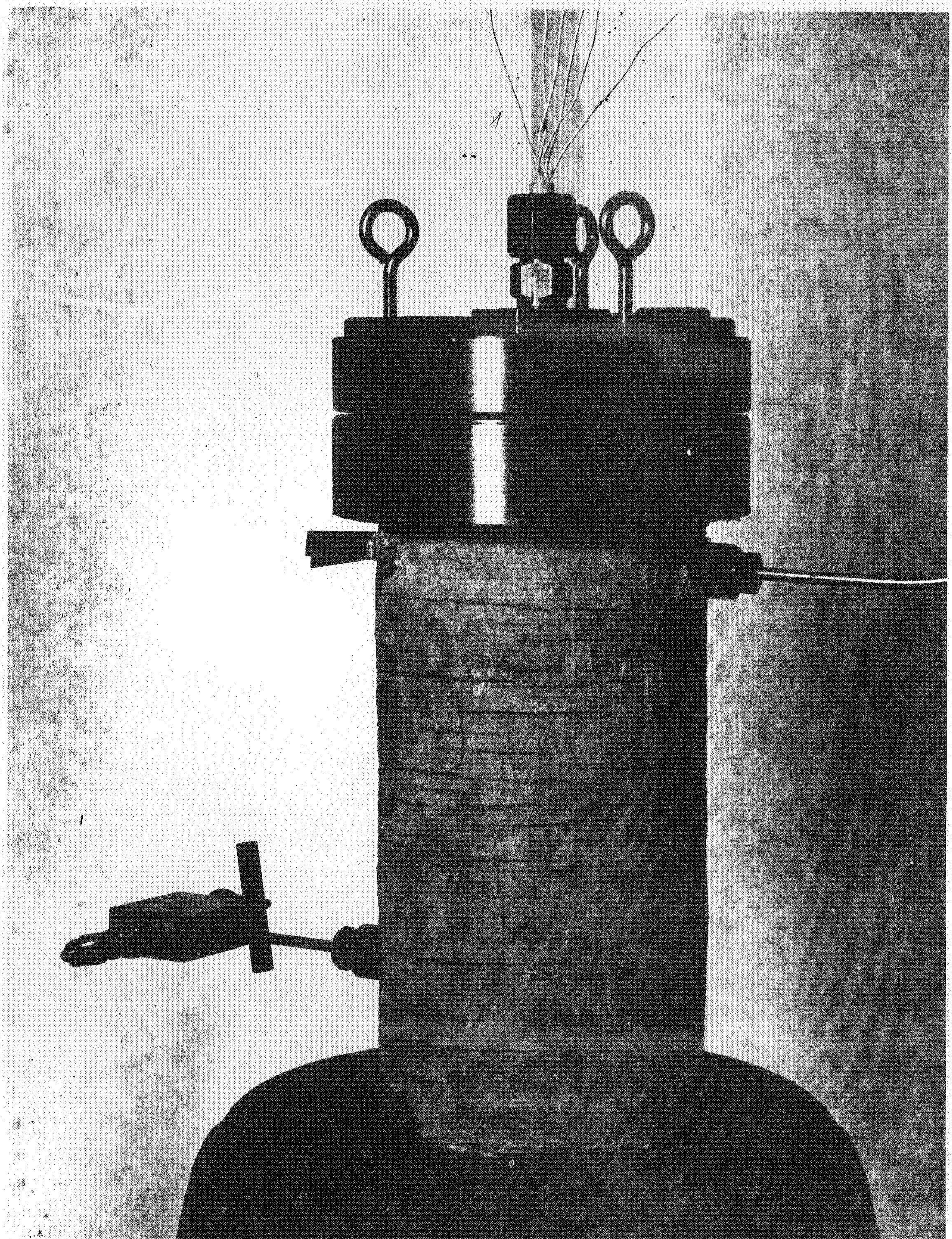


FIGURE 6

Potential "isotherms" for Pd-hydrogen reference electrode at various temperatures (time effects).

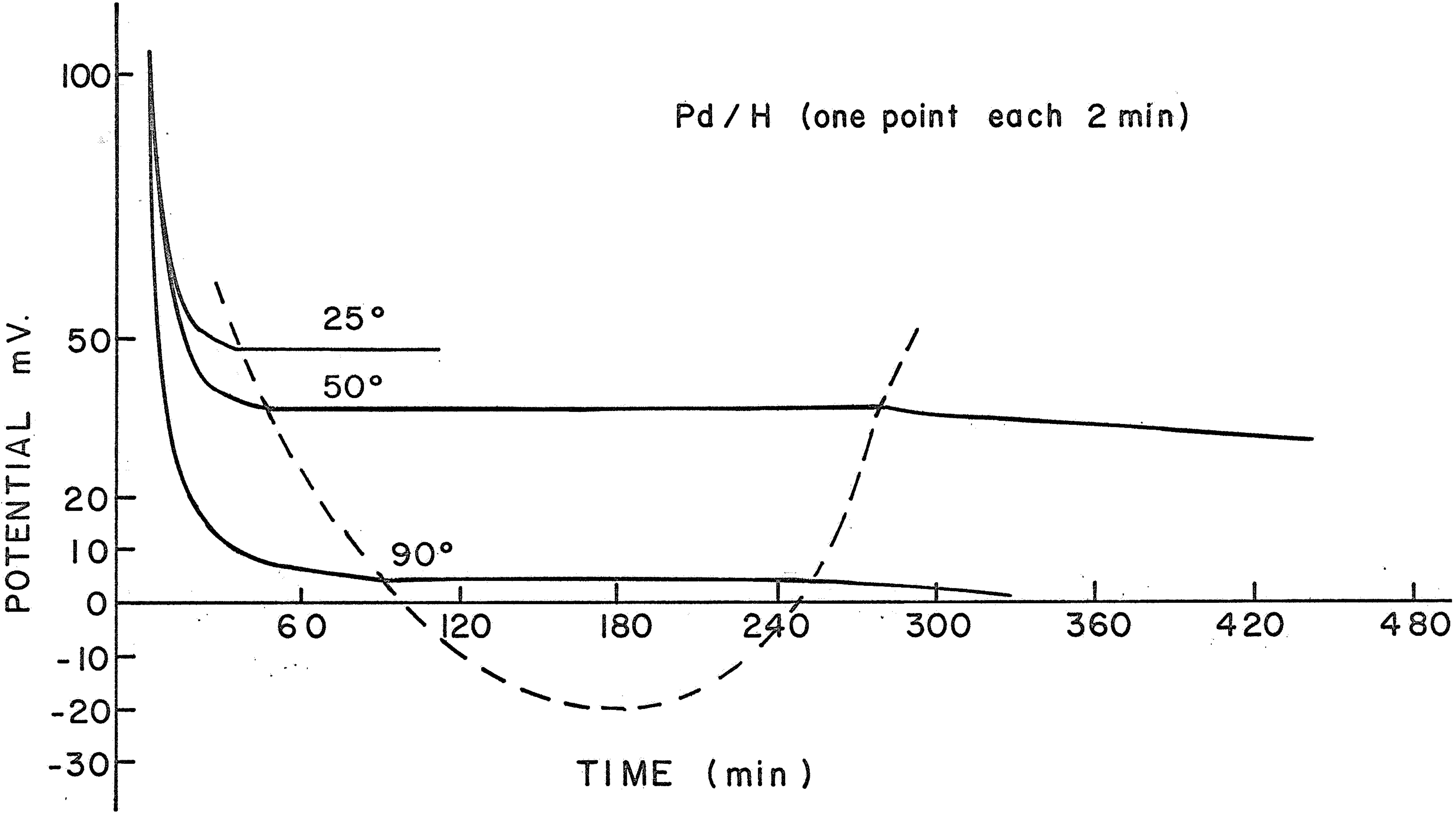

Pd / H (one point each 2 min)
POTENTIAL mV.
100
50
20
10
0
-10
-20
-30
TIME (min)
60
120
180
240
300
360
420
480
25°
50°
90°

FIGURE 7

Variation of Pd-H electrode potential with temperature in 1N $HClO_4$.

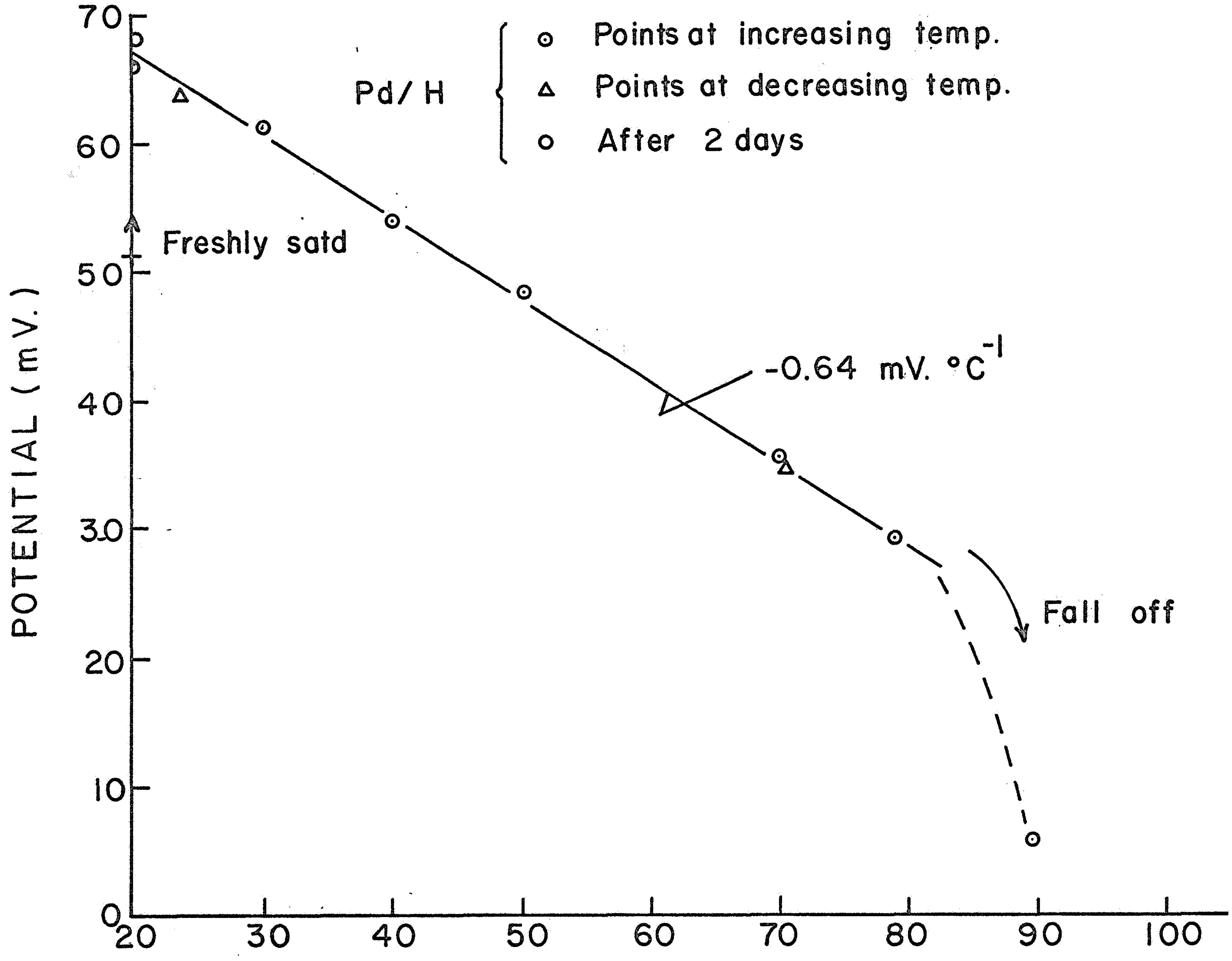
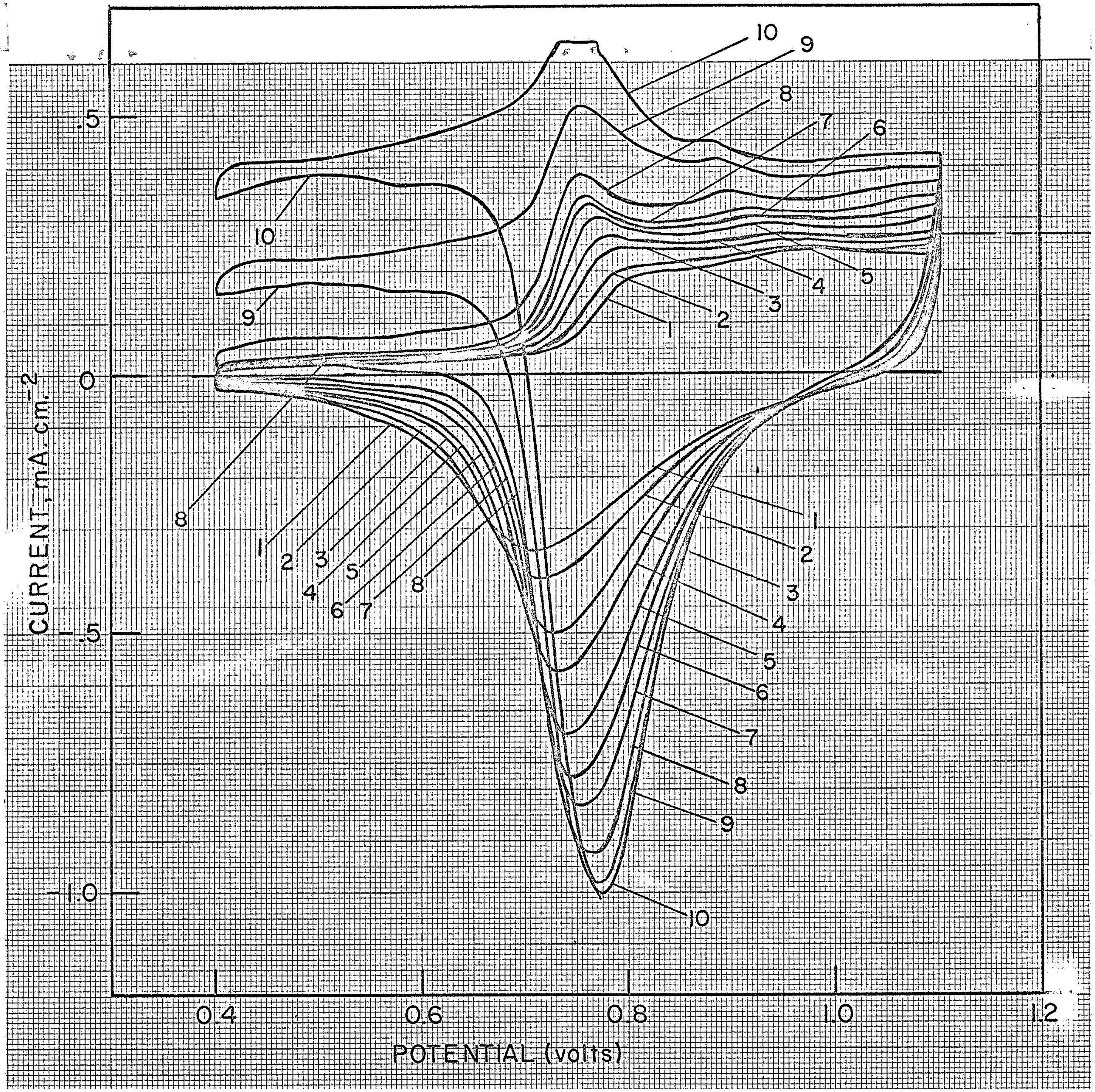

Pd/ H
⊙ Points at increasing temp.
△ Points at decreasing temp.
○ After 2 days
Freshly satd
-0.64 mV. °C-1
Fall off
POTENTIAL (mV.)
70
60
50
40
30
20
10
0
20
30
40
50
60
70
80
90
100

FIGURE 8

Preliminary reduction profiles for surface oxide at Pt electrode over a range of temperatures:

1. 20°C
2. 40°C
3. 60°C
4. 80°C
5. 100°C
6. 120°C
7. 140°C
8. 160°C
9. 180°C
10. 190°C



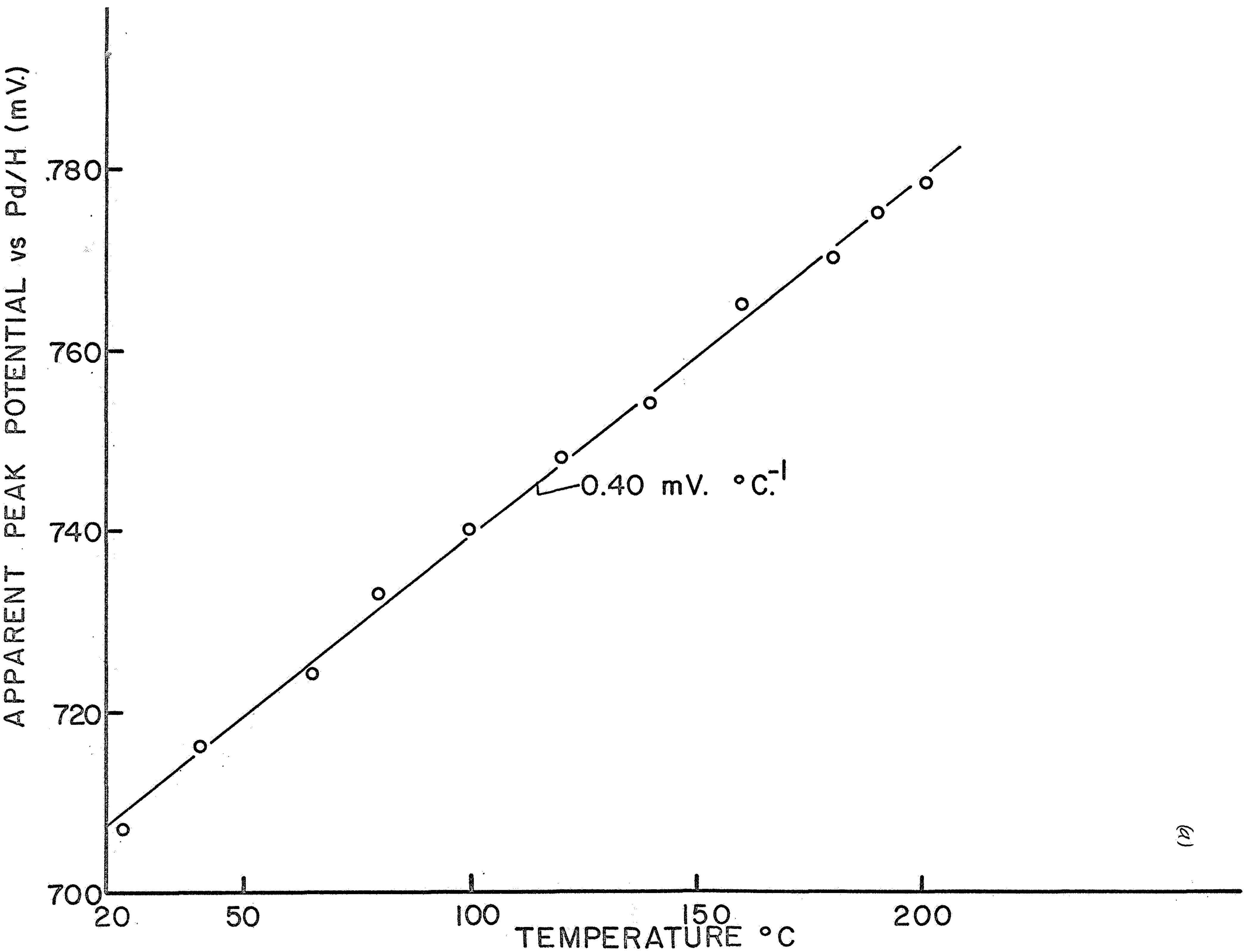
CURRENT, mA. cm.$^{-2}$
.5
0
-.5
-1.0
POTENTIAL (volts)
0.4
0.6
0.8
1.0
1.2
10
9
8
7
6
5
4
3
2
1
10
9
8
1
2
3
4
5
6
7
8
1
2
3
4
5
6
7
8
9
10

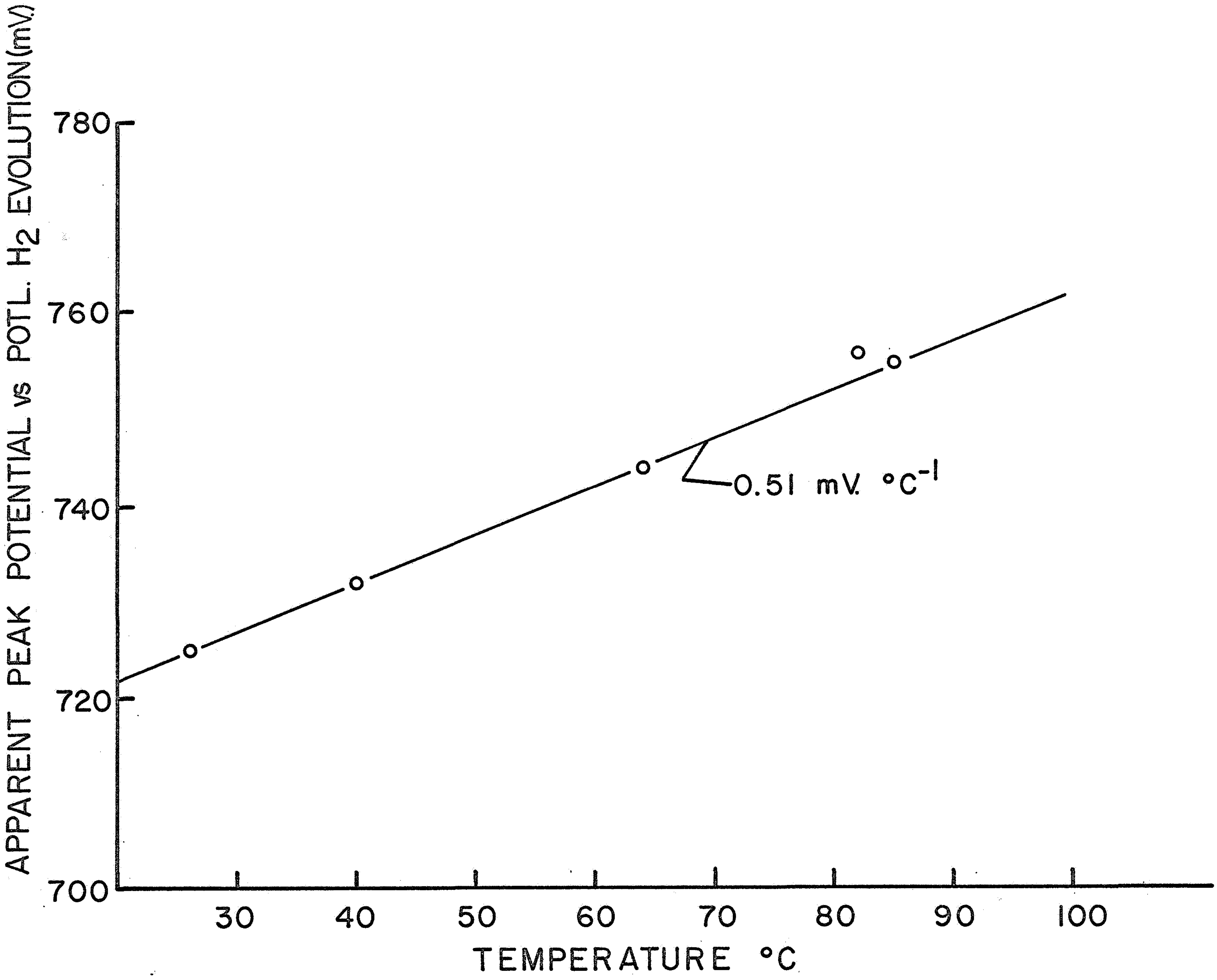
FIGURE 9

Apparent variation of reduction peak potential with temperature:

(a) Pd-H reference potential

(b) Internal H-adsorption reference potential

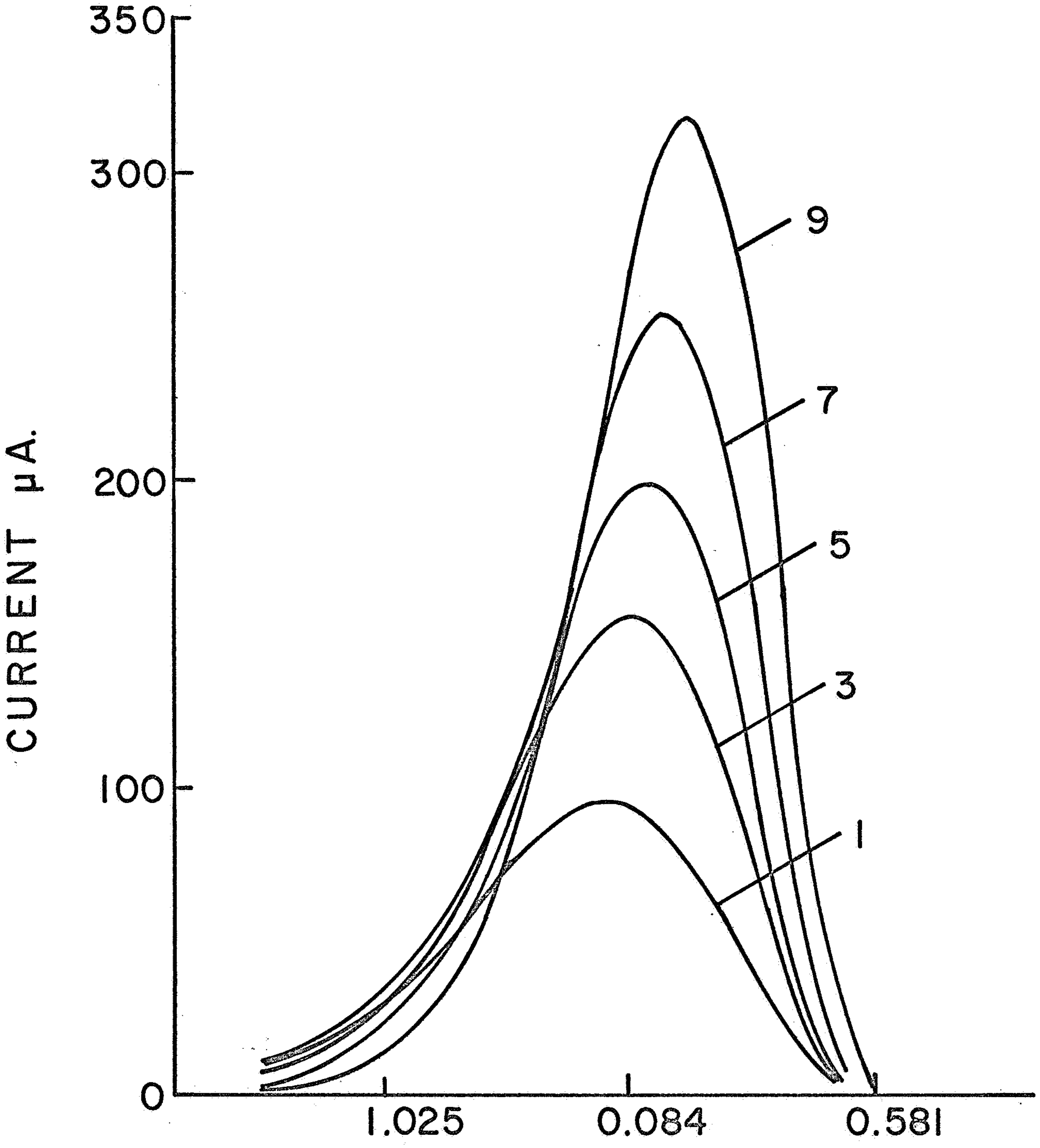

(a)
APPARENT PEAK POTENTIAL vs Pd/H (mV.)
780
760
740
720
700
20
50
100
150
200
TEMPERATURE °C
0.40 mV. °C.$^{-1}$


APPARENT PEAK POTENTIAL vs POTL. H2 EVOLUTION (mV)
780
760
740
720
700
30
40
50
60
70
80
90
100
TEMPERATURE °C
0.51 mV. °C-1

(b)

FIGURE 10

Curves of best fit for the experimental data at smooth Pt (Fig. la) based on equation 3 using first term but for a cathodic process. Numbers refer to comparison with experimental curve numbers in Fig. la.


350
300
200
100
0
CURRENT μA.
1.025
0.084
0.581
POTENTIAL E_H (V)
9
7
5
3
1